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PRELIMINARY MINERALOGICAL EXAMINATION OF A GERMANIUM PROSPECT FROM LANG CREEK, POWELL RIVER AREA, BRITISH COLUMBIA

L.J. Cabri
Mineralogy Section
Mineral Processing Laboratory

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by

L.J. Cabri*

SUMMARY

Sedimentary coal-bearing samples from near Lang Creek, Powell River area, B.C., were found to contain variable quantities of Ge and Ga. The Ge content ranged from <5 to 91 ppm and Ga from 14 to 28 ppm. Mineralogical studies showed that the Ge is most likely, but without absolute certainty, organically bound in the coal. Mass balance calculations support, but do not prove, that the Ge is entirely organically bound. One sample with 2.3% coal contains two coal varieties: a vitrinite with about 0.35 wt % Ge (range 0.18 -0.52), occurring in variably sized irregular lenses and seams up to about a cm thick, and another maceral occurring as irregular disseminations, rarely >50 microns in thickness, and containing less Ge (<0.11 to 0.38%). The finer-grained disseminated maceral may cause potential recovery problems because of intergrowths and friability.

*Research Scientist, Mineralogy Section, Mineral Sciences Laboratories, CANMET, Energy, Mines and Resources Canada, Ottawa K1A 0G1

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INTRODUCTION

Mr. Lauch F. Farris, President of Fargo Oil Corporation, 850 West Hastings Street, Vancouver, B.C. V6C 1E1, requested CANMET's help in characterizing samples (from the Lang Bay prospect, Powell River area, B.C.) by mineralogical and analytical techniques. This was necessary to establish the nature and quantities of valuable constituents as a preliminary investigation to possible eventual exploitation. Mr. Farris referred to earlier work which had indicated the presence of Ge "in the range of 100 gms per short ton" and, by qualitative analysis, of V, In, and Ga. CANMET agreed to conduct Ge, In and Ga analyses on sixteen samples and to perform a mineralogical examination of those samples showing significant values of these elements.

SAMPLES

A total of 58 bagged samples were received on the 17th September, 1981. This was in excess of what Mr. Farris had estimated (letter of Aug. 19, 1981 to W.A. Gow), i.e. "... you can expect to receive sixteen samples of 25 lbs. each for a total weight of 400 lbs. In addition, Mr. Hilchey has suggested that a fist size sample from each zone also be sent." The samples received are listed in Table 1 and a location map is given in the Appendix.

TABLE 1. Samples received

No.	Area*	Description*	Contents**
98801	3	Specimen. Red-bed-upper and lower contacts	Hand specimens
98802	3	Specimen. "Vitrain" up to 1 inch thick in grey arkosic sandstone above red bed.	Hand specimens
98803	3	Sample A. Red-bed-18" thick-channel	∿½" chips
98803	3	" " " "	∿100 mesh
98804	3	" " " "	∿½" chips
98804	3	" " " "	∿100 mesh
98805	3	" " " "	∿½" chips
98805	3	" " " "	∿100 mesh
98806	1	Sample B. Brown-bed-52" thick-channel sample - centre of three cuts	∿½" chips
98806	1	" " " " " "	∿100 mesh
98807	1	" " " " " "	∿½" chips
98807	1	" " " " " "	∿100 mesh
98808	1	" " " " " "	∿½" chips
98808	1	" " " " " "	∿100 mesh
98809	1	Specimen. Typical brown-bed material (Sample B)	Hand specimens
98809	1	- " " " "	∿½" chips
98809	1	- " " " "	∿100 mesh
98810	1	Sample C. Brown-bed-60" thick-channel sample base of brown-bed not exposed - westerly of three cuts	∿½" chips
98810	1	" " " " " "	∿100 mesh
98811	1	" " " " " "	∿½" chips
98811	1	" " " " " "	∿100 mesh
98812	1	" " " " " "	∿½" chips
98812	1	" " " " " "	∿100 mesh
98813	1	" " " " " "	∿½" chips
98813	1	" " " " " "	∿100 mesh
98814	1	Sample D. Arkose overlying Sample C with thin, discontinuous coaly material - 20" channel sample	∿½" chips
98814	1	" " " " " "	∿100 mesh
98815	1	Sample E. Brown-bed - same material as Sample C - Grab sample from dump	∿½" chips
98815	1	" " " " " "	∿100 mesh
98816	1	" " " " " "	∿½" chips
98816	1	" " " " " "	∿100 mesh
98817	1	" " " " " "	∿½" chips

* Taken from report by G.R. Hilchey (8 Sept. 1981); ** General appearance on arrival.

(Table 1 - cont.)

No.	Area*	Description*	Contents**
98817	1	Sample E. Brown-bed - same material as Sample C - Grab sample from dump	∿100 mesh
98818	1	" " " " " "	∿½" chips
98818	1	" " " " " "	∿100 mesh
98819	1	" " " " " "	∿½" chips
98819	1	" " " " " "	∿100 mesh
98820	1	" " " " " "	∿½" chips
98820	1	" " " " " "	∿100 mesh
98821	1	" " " " " "	∿½" chips
98821	1	" " " " " "	∿100 mesh
98822	1	" " " " " "	∿½" chips
98822	1	" " " " " "	∿100 mesh
98823	1	" " " " " "	∿½" chips
98823	1	" " " " " "	∿100 mesh
99924	1	" " " " " "	∿½" chips
98824	1	" " " " " "	∿100 mesh
98825	1	" " " " " "	∿½" chips
98825	1	" " " " " "	∿100 mesh
98826	2	Sample F. Brown-bed- grab of typical material from dump (cut was unsafe)	∿½" chips
98826	2	" " " " " "	∿100 mesh
98827	2	" " " " " "	∿½" chips
98827	2	" " " " " "	∿100 mesh
98828	2	" " " " " "	∿½" chips
98828	2	" " " " " "	∿100 mesh
98829	2	" " " " " "	∿½" chips
98829	2	" " " " " "	∿100 mesh
-	2	Specimen. Typical brown-bed material (Sample F)	Hand specimens

* Taken from report by G.R. Hilchey (8 Sept. 1981); ** General appearance on arrival.

SAMPLE PREPARATION AND METHOD OF INVESTIGATION

The unexpected large number of samples received required consultation with Mr. Farris, who agreed to grouping of ∿ 100 mesh samples 98803-05 (=Sample A), 98806-08 (=Sample B), 98810-13 (=Sample C), 98815-25 (=Sample E), and 98826-29 (=Sample F). These combined samples, as well as the ∿100 mesh portion of sample 98814 (=Sample D), were reground to minus 200 mesh. These six samples were submitted for quantitative spectrographic analysis for Ge, Ga and In. Samples B and F had the highest values and their original uncombined ∿½" fractions were crushed and ground to minus 200 mesh: i.e. samples 98806-08 and 98826-29. These were also submitted for quantitative spectrographic analysis for the same elements plus V. The sample with the highest values was then examined mineralogically by binocular and ore microscopes, with a scanning electron microscope and analysed with an electron microprobe and by X-ray powder diffractometry. The carbon content of a sample was determined by two methods: Low Temperature Plasma Ashing (LTA) and by conventional proximate analysis.

RESULTS

1. Mineralogy

Examination of the hand specimens under a binocular microscope revealed that the samples are carbonaceous sedimentary rocks. The "Brown Beds" appear to be a dark-grey carbonaceous argillaceous sandstone with variable clay/quartz ratio. The carbonaceous material is irregularly distributed in the sandstone matrix in the form of millimetre to over one centimetre-thick seams of vitrinite, but these are discontinuous along strike and in the planar dimension (Fig . 2 and 3).

The vitrinite is typically bright in appearance and breaks easily with a concoidal fracture (Fig. 3) indicating relatively easy liberation from the matrix. In polished section the vitrinite generally has a low to nil pyrite content, but some grains have a moderate quantity (est. ~5%) of pyrite inclusions (Fig . 4, 5 and 6). Dispersed throughout this sandstone-clay matrix there occur thiner micro-seams (Fig. 7) of a less bright coaly substance which also wraps itself around the individual minerals. This coal is also softer and does not have a conchoidal fracture.

The "Upper and lower contact of Red Bed" from Area 3 appears, under the binocular microscope, to consist of dense blue-gray clay with yellow and brown ochre colouration. The specimen labelled "Vitrain" from Area 4, under the binocular microscope, appears to be similar to the "Brown Bed" sample from Area 1 but crumbles easily and maybe contains more vitrinite.

Semi-quantitative X-ray diffraction analysis of minus 40 mesh material from sample 98807 (see Table 1) indicated major quartz, minor kaolinite and possible trace of calcite. Similar analyses of minus 200 mesh material from samples A

and D (see Table 1) gave: Sample A major kaolinite, minor quartz, trace feldspar; Sample D major quartz, moderate kaolinite and minor feldspar. This suggests that the field descriptions of "Brown Bed" represent an argillaceous and carbonaceous sandstone and that "Red Bed" may represent a more argillaceous member grading to kaolinite clay at the upper and lower contacts. The sample described as arkose is probably that and no carbonaceous matter was seen in it.

2. Bulk analysis

The combined samples (A,B,C,D,E, and F) were first submitted for quantitative spectrochemical analysis and the subsamples for the two highest in Ge (B and F) were resubmitted for analysis. The analyses are detailed in Table 2, below, and include analyses for Ga, In and V. The precision is estimated to be ±15%.

TABLE 2. Spectrographic analyses

	Elements (ppm*)			
Sample	Ge	Ga	In	V
A (Red Bed)	<5	25	<10	nd**
B (Brown Bed)	57	28	<10	nd
C (U. Brown Bed)	<5	26	<10	nd
D (Arkose)	<5	15	<10	nd
E (Brown Bed dump)	<5	28	<10	nd
F (Brown Bed dump)	51	25	<10	nd
98806	41	17	<10	107
98807 Sample B	91	23	<10	108
98808	77	20	<10	118
98826	34	19	<10	72
98827 Sample F	85	14	<10	66
98828	30	16	<10	64
98829	38	16	<10	75

*ppm = micrograms metal per gram of sample, 10^{-6} g/g; 1 ppm is equivalent to 0.03215 troy ounce per tonne.
**nd = not determined

3. Ore microscopy and in situ analyses

Sample 98807 was selected for more detailed mineralogical examination under reflected light because it had the highest Ge content. Sedimentary fragments were found to contain thin (usually <50 μm) discontinuous sinuous lenses of coal, usually in a clay matrix (Fig. 8). These were difficult to analyse with the electron probe because the expanded beam (~25 μm) required for such analyses had to be fit within the individual seams. The Ge content of this coal variety varied between less than the Minimum Detection Limit (MDL), calculated to be 0.11 wt %, to a high value of 0.38% (Table 3). The average for this type of coal, however, is probably less than 0.15 wt. % Ge. Occasional grains of pyrite and, more rarely, tennantite [$(Cu,Fe)_{12}As_4S_{13}$] were found included in the quartz or clay, but no Ge could be detected in either sulphide (MDL for Ge in pyrite was 0.03 wt %).

Vitrinite from sample 98807 was handpicked and mounted separately for examination with the ore microscope. While many grains were entirely free of pyrite inclusions (Fig. 4), others had a variable quantity (Fig. 5 and 6) with an estimated maximum content of about 5%.

Germanium analyses of the vitrinite ranged from 0.18 wt % to 0.52 wt % with an arithmetic average of 0.35 wt % Ge for the ten grains analysed (Table 3). Determination of carbon content by two methods (LTA and proximate analysis) gave very similar results of 2.36 and 2.25%, respectively (Table 4). The LTA determination is arrived at by weight loss after removal of adsorbed moisture. A coal content of 2.1% is therefore a reasonable figure for sample 98807.

TABLE 3

Electron-probe analyses for Ge in coal

Thin interstitial coal

Grain	No. spots*	Average wt %	Range**
A	8	0.12	<MDL† to 0.26
B	4	0.17	0.11 to 0.23
D	5	<MDL	<MDL
E	8	0.15	<MDL to 0.27
6	5	0.15	<MDL to 0.25
1	10	0.10	<MDL to 0.18
2A	5	<MDL	<MDL
2B	3	0.11	-
3	2	0.38	-
4	2	0.13	-
Vitrinite			
A	8	0.18	<MDL to 0.36
B	8	0.37	0.28 to 0.46
C	8	0.24	0.15 to 0.30
D	8	0.29	0.18 to 0.45
E	8	0.41	0.30 to 0.49
F	8	0.39	0.26 to 0.48
G	8	0.37	0.35 to 0.43
H	8	0.44	0.33 to 0.54
I	8	0.35	0.24 to 0.44
J	8	0.52	0.43 to 0.59

* No. spots = number of spot analyses
** range could not be determined for 3 or less spot analyses
† MDL = Minimum Detection Limit of 0.11 wt % Ge. Note values for MDL were taken as zero when averaging.

TABLE 4

Results of LTA and proximate analysis

Carbon Content	LTA*	2.36%
	Proximate	2.25%
Hydrogen	"	0.7%
Nitrogen	"	0.2%

*After 24 hours in a vacuum dessicator with a loss of 0.41% adsorbed moisture. Temperatures monitored at 60-75°C for total 66 hours.

DISCUSSION

The two elements of potential economic interest (as determined by quantitative spectrographic analyses) are Ge and Ga, but the values obtained for the latter did not justify further study in the present investigation. The literature on germanium in coal is voluminous and there appears to be much evidence that germanium is organically bound in coal, though Ge has also been found in some of the mineral inclusions (e.g. sphalerite, pyrite, clay minerals). There also appears to be general agreement in the literature that much of the germanium in coal is of secondary origin such as produced by a process of absorption from percolating solutions. This has resulted in the common occurrence of germanium concentrations at the tops and bottoms of coal beds.

In situ analyses of coal by electron probe indicated organically bound Ge with variable Ge content, apparently dependent on the type of coal. The Ge values obtained by these in situ analyses appear to be qualitatively consistent with the presumption that all, if not most of the Ge, is organically bound. A search for inorganic mineral hosts for Ge was unsuccessful, but this was not exhaustive in view of the apparent reasonableness of results obtained from the in situ electron-probe analyses.

It is not possible at this time to determine the proportion of the vitrinite with the high Ge content relative to the coal with low Ge content. Bulk analysis of sample 98807 gave 91 ppm ± 15% Ge (or 0.009%) and, therefore, based on a carbon content of 2.3%, the average Ge content of both coal varieties should be about 0.40%, with a range between 0.33 and 0.45%. This appears to be reasonable in view of the fact that the electron-probe analyses for vitrinite

averaged 0.35% and ranged between 0.18 and 0.52%. The other coal variety had a range of values from less than 0.11 to 0.38%.

The coal content in sample 98807 is less than for the sample studied by Farand and Puddington (1969) in their oil-phase agglomeration tests (10% coal). They also reported that "The composition of the ore varies considerably, but it would appear from data available that the carbonaceous material, whether massive or scattered throughout the sandstone matrix, comprises about 10% of the ore and contains up to 0.4 per cent germanium, although concentrations of about 0.06 per cent are more common."

The present samples were not identified as to their exact stratigraphic location, and neither was the relation described between channel samples taken at each individual sample site. For example, it is not known whether samples 98806, 98807, and 98808 represent different stratigraphic sections of the 52" thick "Brown Bed", and if so, which specific ones. Maybe this information is known to the company. On the other hand, if this deposit was considered for exploitation, while it is not likely that the mining width be less than a metre it may be important to know more precisely the stratigraphic distribution of the germanium concentration.

Without regard for the economics of extraction of germanium metal and marketability there are two potential problems for exploitation. This preliminary investigation has shown that some of the germanium is finely disseminated in the form of a coal variety that may be difficult to liberate from the host matrix and, even if liberated, may have a tendency to slime when using conventional mineral dressing techniques. The second potential problem, considered to be of lesser probability, requires that a more exhaustive study be made to confirm that all the germanium is organically bound.

The technical assistance of J.M. Beaulne, P. Carrière, R. Horton, J.H.G. Laflamme and E. Murray of MSL and L. Janke of ERL is gratefully acknowledged.

REFERENCE

Farand, J.R. and Puddington, I.E. "Oil-phase agglomeration of germanium-bearing vitrain coal in a shaly sandstone deposit"; Canadian Mining and Metallurgical Bulletin; 62:683:267-271; 1969.

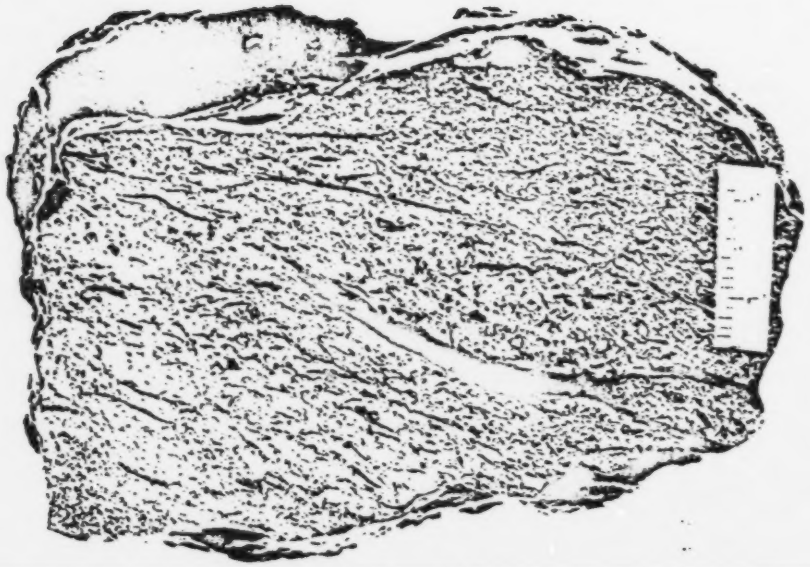


Figure 1. Photograph of polished piece of "Brown-bed" hand specimen from Area 1. The more continuous, and generally thicker coal seams are vitrinite. Scale = cm.

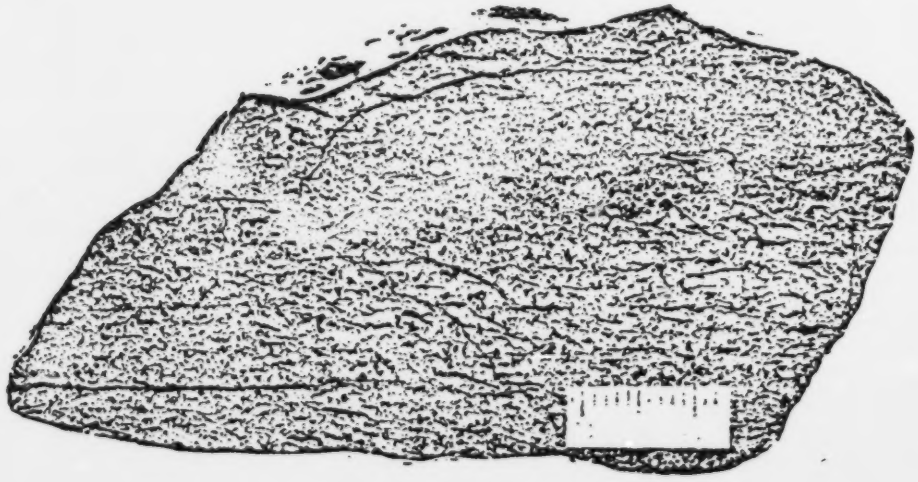


Figure 2. Another hand specimen from the same sample bag as in Figure 1. Scale = cm.

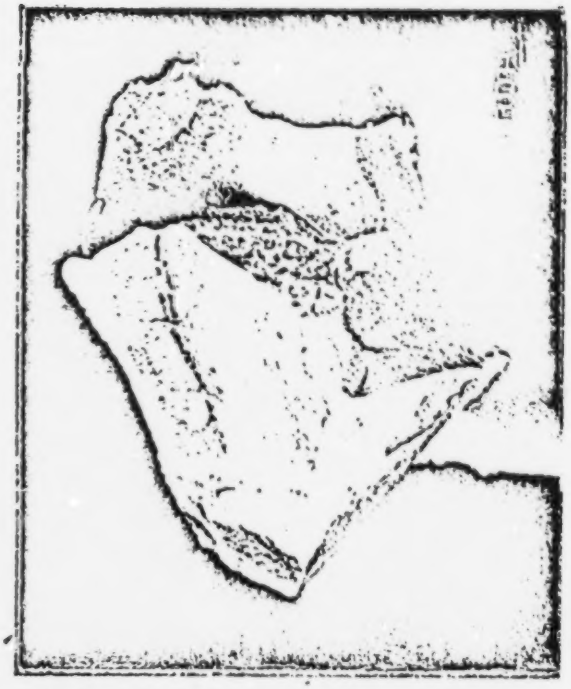


Figure 3. Fragment of easily liberated vitrinite showing conchoidal fracture. SEM micrograph.

Figure 4. Photomicrograph of polished section and vitrinite free of mineral inclusions.

Figure 5. Photomicrograph of polished section of vitrinite with sparse pyrite inclusions.

Figure 6. Photomicrograph of polished section of vitrinite with most abundant pyrite inclusions encountered.

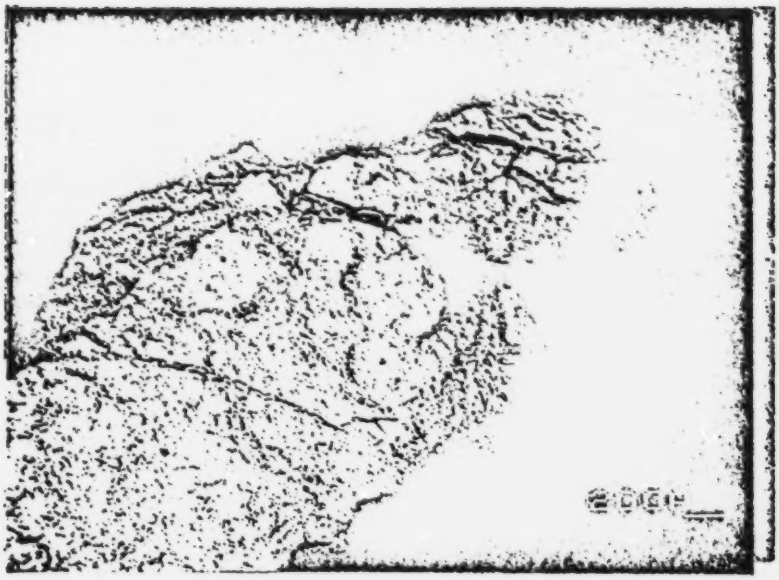


Figure 7. Sedimentary fragment with thin coal seams. SEM micrograph.

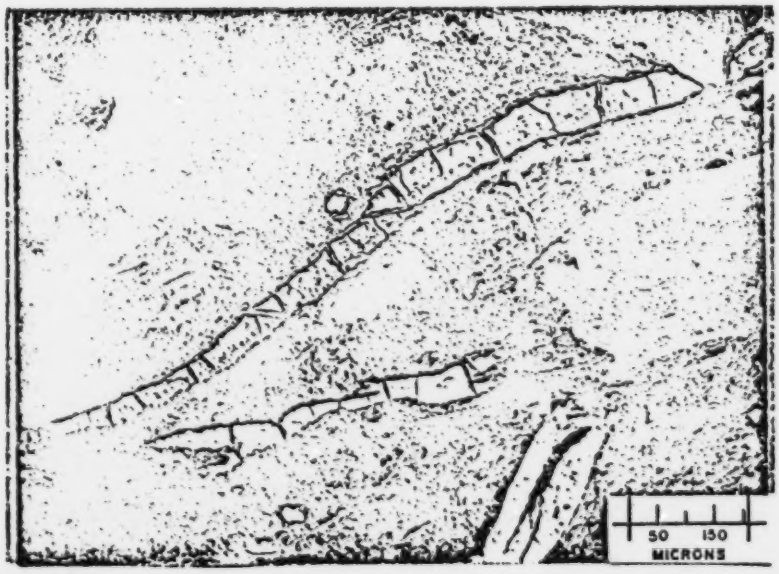
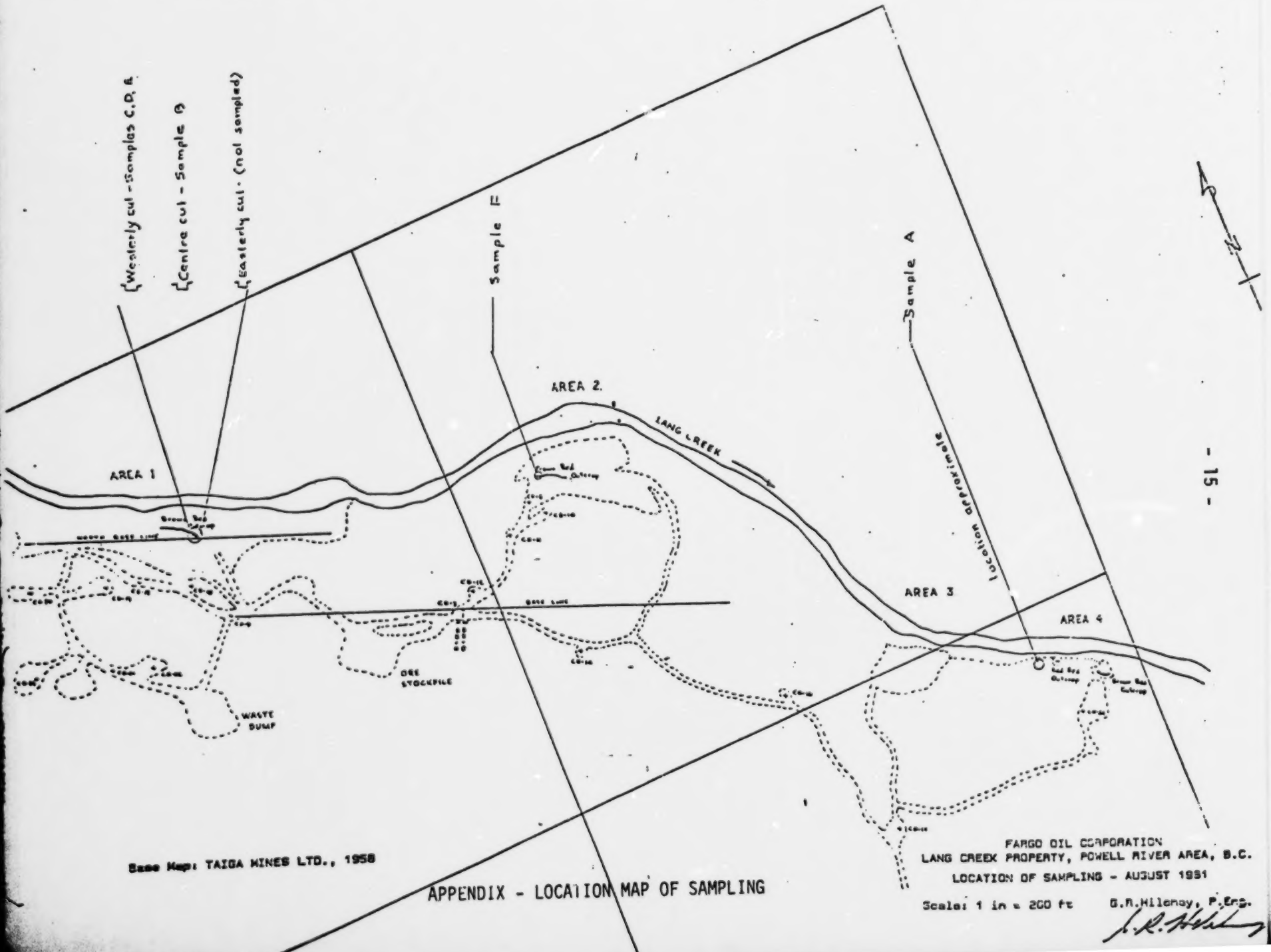


Figure 8. Photomicrograph of polished section showing thin coal seams and streaky lenses in clayey matrix.



APPENDIX - LOCATION MAP OF SAMPLING